

**REMARKS**

Reconsideration and withdrawal of the rejections to the application are respectfully requested in view of the remarks herewith.

**I. STATUS OF THE CLAIMS AND FORMAL MATTERS**

Claims 11-21 are now pending. Claims 11 and 13-20 have been amended, without prejudice, without admission, without surrender of subject matter, and without any intention of creating any estoppel as to equivalents. Claim 21 is added.

No new matter is added.

It is submitted that these claims, as originally and herein presented, are and were in full compliance with the requirements of 35 U.S.C. §112. The amendments and remarks are not added for the purpose of patentability within the meaning of 35 U.S.C. §§101, 102, 103 or 112. Rather, these claims are added for clarification and to round out the scope of protection to which Applicants are entitled.

**II. 35 U.S.C. §112, SECOND PARAGRAPH, REJECTIONS**

Claims 11-20 were rejected under 35 U.S.C. §112, second paragraph, for allegedly being indefinite. The amendments to the claims render the rejections moot.

Consequently, reconsideration and withdrawal of the Section 112, second paragraph, rejections are respectfully requested.

**III. THE ART REJECTIONS ARE OVERCOME**

Claims 11, 12 and 15-20 were rejected under 35 U.S.C. 102(e) as being anticipated by U.S. Patent No. 5,720,872 to Gupta. ("Gupta"). In addition, claims 13 and 14 were rejected under 35 U.S.C. 103(a) as being allegedly unpatentable over Gupta in view of Lacy et al. (US Patent No. 3,314,879) and Egloff (US Patent No. 1,707,349), respectively. Further, claims 11-13 and 15-20 were rejected under 35 U.S.C. 103(a) as being unpatentable over Pruiss (US Patent No. 3,519,557) in view of Mellbom (US Patent No. 3,544,428). Also, claim 14 was rejected under 35 U.S.C. 103(a) as being unpatentable over Pruiss in view of Mellbom, further in view of Egloff. The rejections are traversed. The cited documents, either alone or in combination fail to

disclose, teach, suggest, enable, or provide the motivation for a skilled artisan to practice the instantly claimed invention.

The present application claims priority to French Patent Application No. 96/16290, filed on December 31, 1996. A verified English translation of this French priority application is enclosed. By the verified English translation and remarks herewith, it is clear that the present application is entitled to its priority filing date December 31, 1996; and, it is respectfully requested that the present application be fully accorded its priority filing date of December 31, 1996.

Gupta issued from USSN 08/775,638, filed December 31, 1996. Gupta is not available against the present application. The present application has an effective filing date of December 31, 1996; an effective filing date the same as the US filing date of Gupta. Ergo, Gupta is not prior art as to the present application.

Reconsideration and withdrawal of the rejections under 35 U.S.C. §§ 102(e) and 103 as to Gupta are respectfully requested.

In addition, claims 11-13 and 15-20 were rejected under 35 U.S.C. 103(a) as being unpatentable over Pruiss in view of Mellbom. Further, claim 14 was rejected under 35 U.S.C. 103(a) as being unpatentable over Pruiss in view of Mellbom, further in view of Egloff.

It is respectfully pointed out that any combination of these three disparate documents would not have motivated or led a skilled artisan to practice the instantly claimed invention. None of Pruiss, Mellbom, or Egloff, either alone or in any combination, teach, disclose, suggest or motivate a skilled artisan to an apparatus for hydrotreating a hydrocarbon feedstock, comprising, *inter alia*, a fractionation unit containing an internal partitioning structure defining two distinct injection zones in flow communication with a common upper vaporization zone.

It is respectfully emphasized that Pruiss fails to teach or suggest, *inter alia*, a fractionation unit containing an internal partitioning structure defining two distinct injection zones in flow communication with a common upper vaporization zone, as admitted by the Examiner (*Office Action* at 8). Mellbom does not remedy this deficiency. A skilled artisan would readily understand that these two references cannot be combined.

It is respectfully asserted that the allegations in the Office Action, that a skilled artisan, reading, *inter alia*, Pruiss and Melbom, would be motivated to practice the instantly claimed invention are incorrect. Indeed, Pruiss relates to a liquid-phase hydrogenation process in a

plurality of stages wherein high temperature and high pressure flashes are carried out in between the hydrogenation stages whereby low boiling materials are removed and the temperature of the reaction is decreased (column 2, lines 30-36). The pressure in the hydrogenation steps varies from 400 to 4000 psig (column 2, line 57-58) and the flashing zones are at a pressure of not more than 100 pounds less than the pressure employed in the hydrogenation zones (column 2, lines 38-40). The pressure in the flashing zone therefore is at least 300 psi (approximately 20 atm).

Melbom relates an apparatus for distilling hydrocarbons. Hydrocarbons are generally distilled at atmospheric pressure or reduced pressure but never at high pressure. The distillation process of Melbom works at reduced pressure. As a matter of fact, it is clearly specified at column 3, line 71 that “[b]oth flashing sections 4 and 8 are held at an absolute pressure of 1.6 inches Hg”. (Co. 3, lines 69-72). (1.6 inches Hg = 0.05 atm).

More specifically, the flash tower of Pruiss functions at a pressure (20 atm) approximately 400 times higher than the pressure (0.05 atm) of the distillation apparatus provided in Mellbom; the flash tower of Pruiss is not analogous to the distillation apparatus of Mellbom. Accordingly, one skilled in the art would not be motivated to combine the teachings of Pruiss and Mellbom to arrive at the instant invention.

Further, Egloff does not remedy the deficiencies noted above, *i.e.*, that neither Pruiss nor Mellbom teach or suggest an apparatus for hydrotreating hydrocarbon feedstock comprising, *inter alia*, a fractionation unit containing an internal partitioning structure defining two distinct injection zones in flow communication with a common upper vaporization zone as Egloff does not teach or suggest such an apparatus containing such a fractionation unit.

Thus, a skilled artisan would not be motivated to practice Applicants’ invention by virtue of any reading of Pruiss in combination with in view of Melbom, further in view of Egloff.

It is respectfully submitted that the rejection is based on impermissible picking and choosing of portions of three disparate references; three references that a skilled artisan knows cannot be combined. As the requisite suggestion or motivation to combine the cited references is clearly absent, a skilled artisan would have lacked the incentive to practice Applicants’ invention. *In re Laskowski*, 12 U.S.P.Q. 2d 1 397, 1399 (Fed. Cir. 1989); *In re Obukowitz*, 27 U.S.P.Q. 2d 1063 (BOPAI 1993).

The Examiner is respectfully reminded that for the Section 103(a) rejection to be proper, both the suggestion and the expectation of success must be found in the prior art, and not in

Applicants' own disclosure. *In re Dow*, 5 U.S.P.Q.2d 1529, 1531 (Fed. Cir. 1988). Indeed, hindsight based on Applicants' own success as disclosed and claimed in the present application, is not a justifiable basis on which to contend that the ultimate achievement of the present invention would have been obvious at the time the invention was made. *In re Fine*, 5 U.S.P.Q.2d 1596, 1599, 1600 (Fed. Cir. 1988).

Further, "obvious to try" is not the standard upon which an obviousness rejection should be based. *Id.* And as "obvious to try" would be the only standard that would lend the Section 103 rejections any viability, it is respectfully submitted that the rejections must fail as a matter of law. Therefore, applying the law to the instant facts, the rejections are fatally defective and should be removed.

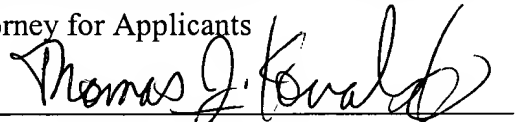
Consequently, reconsideration and withdrawal of the Sections 102 and 103 rejections are in order and such actions are respectfully requested.

**CONCLUSION**

The Amendments, remarks herein, and enclosure herewith place the application in condition for allowance. Early and favorable reconsideration of the application and prompt issuance of a Notice of Allowance are earnestly solicited.

Respectfully submitted,

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**INPI**

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**CERTIFICATES OF UTILITY - CERTIFICATES OF ADDITION**

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The Director-General of the National Institute for Industrial Property certifies that the attached document is a certified copy of an application for an industrial property right submitted to the Institute.

Given in Paris, 22nd DEC., 1997

For the Director-General of the  
National Institute for Industrial Property  
Head of the Department

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## APPLICATION FOR GRANT

Confirmation of faxed submission ☐

To be completed in black ink in capital letters

DATE OF DELIVERY OF DOCUMENTS

31 DEC. 1996

1

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NATIONAL REGISTRATION NUMBER DATE OF APPLICATION

96 16290

31 DEC. 1996

2

APPLICATION for a  
patent of invention

NO. OF GENERAL POWER

CORRESPONDENT'S REFERENCE

37246/1348/DS/MIB

CORRESPONDENT'S TEL. NO.

48 74 92 18

Establishing of the search report ☒ immediately

TITLE OF THE INVENTION

Hydrotreating process for a hydrocarbon charge and apparatus for applying said process.

3 APPLICANT(S): Surname and first names (underline family name), or designation and legal form

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4 INVENTOR(S) The inventors are the applicants

☒ No

5 REDUCTION IN FEES

6 STATEMENT OF PRIORITY OR CLAIMING THE DATE OF AN EARLIER APPLICATION

COUNTRY OF ORIGIN

NUMBER

DATE OF APPLICATION

NATURE OF APPLICATION

7 DIVISIONS PRIOR TO PRESENT APPLICATION

8 SIGNATURE OF APPLICANT OR AGENT

SIGNATURE OF RECEIVING OFFICIAL

SIGNATURE AFTER RECORDAL OF APPLICATION

NAME AND CAPACITY OF SIGNATORY

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DEPARTMENT FOR THE ADMINISTRATION OF PATENTS

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96 16290

TITLE OF THE INVENTION:

Hydrotreating process for a hydrocarbon charge and apparatus for applying said process.

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**NOTE:** By way of exception, the name of the inventor may be followed by the name of the company when the latter is not the same as the applicant company.

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Date and Signature(s) of the Applicant(s) or of the Agent

24th January, 1997

(Signature)

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CPI 92.1122

## **HYDROTREATING PROCESS FOR A HYDROCARBON CHARGE AND APPARATUS FOR APPLYING SAID PROCESS**

The present invention relates to a hydrotreating process for a hydrocarbon charge, using at least one hydrotreating reactor, and to an apparatus for applying said process.

Hydrotreating or hydrorefining processes have assumed very considerable importance in the refining of petroleum products; petroleum and petroleum fractions are highly complex mixtures in which are contained, in respect of the hydrocarbons, various compounds principally containing sulphur, nitrogen, oxygen and metals such as, in particular, nickel and vanadium; the quantity and nature of these compounds varies depending on the source of the crude oil; these are impurities which have an adverse effect on the good quality of petroleum products, owing to pollution, corrosion, odour or stability.

Hydrotreating reactions include, principally, hydrodesulphurization (HDS), hydrodenitriding (HDN), hydrodeoxygenation (HDO), hydrodemetallization (HDM), as well as the hydrogenation of unsaturated groups (olefins, aromatics) and hydrocracking; these reactions are carried out in the presence of specific catalysts, in particular oxide-based or metal-sulphide-based catalysts, such as cobalt, nickel or molybdenum on an aluminium oxide support, at high hydrogen pressures and at high temperatures ( $> 300^{\circ}\text{C}$ ).

A description of the industrial conditions for the application of hydrorefining processes and, in particular, for hydrodesulphurization is to be found, for example, in Volume 1 of the book by P. Wuithier, published by Technip and entitled "Le pétrole, raffinage et génie chimique", pages 816 to 831.

The petroleum industry is faced, more particularly, with the problem of eliminating the sulphur compounds contained in the crude oils used in refining, since these may have a sulphur content (in % by mass) of between 0.14 and 0.8 % in respect of crude oils having a low sulphur content (BTS), and between 1.75 and 2.5 % in respect of crude oils having a medium or high sulphur content (MTS and HTS); from this, it follows that the different products obtained from the direct distillation of such a crude oil, or from a treatment specific thereto or to its distillates (for example



pyrolysis, thermal cracking or catalytic cracking), have a sulphur content which is incompatible with the specifications or the standards applied in industrial countries.

Hydrodesulphurization reactions are characterized by the rupture of the C-S bond of the sulphur derivatives contained in crude oils, i.e. mercaptans, sulphides and thiophenic compounds; sulphur is eliminated by chemical combination with hydrogen in order to form hydrogen sulphide  $H_2S$ ; the desulphurization reactions are complete (not in equilibrium), exothermic, consume hydrogen, and slow in respect of the aromatic compounds; the most widely used industrial catalysts are of the Co-Mo (cobalt-molybdenum) type and Ni-Mo (nickel-molybdenum) type on an aluminium-oxide support.

It is possible for the charges or petroleum fractions to be treated according to the present invention, to vary and to comprise, for example, in particular:

- tops from atmospheric distillation, such as liquid petroleum gas (GPL) and light petrol (the range of boiling temperatures of which is between 0 and 80-100° C) and which has a low sulphur content, the elimination of which is simple;
- heavy petrols (boiling temperature between 100 and 185° C) intended for catalytic reforming using catalysts which are highly sulphur-sensitive, as well as petrol from catalytic cracking;
- the kerosene fraction (185 to 220-240° C) used for preparing aviation fuel and containing mercaptans and thiophenes, is treated by sweet hydrotreating or sweetening, for example according to the MEROX process (oxidation of the mercaptans);
- the gas oil fractions (240 to 370° C) mainly intended for preparing diesel fuel and domestic oil fuel and containing, in particular, benzothiophenes and dibenzothiophenes (320-370° C for the heavy gas oil fraction) which are increasingly difficult to eliminate;
- vacuum distillate fractions, highly refractory to desulphurization.

A known process for the desulphurization of hydrocarbons, such as gas oils, when applied industrially generally comprises the following steps: the charge is mixed with treatment gas rich in hydrogen and pre-compressed, this mixture is heated by a furnace and is introduced at about 350° C into a reactor which is provided with a fixed bed of catalyst of the Co-Mo type, at a pressure of about 50 bars and a partial hydrogen pressure of 30 bars; the reaction effluent, comprising liquid and gas, is directed to a high-pressure separator so as to recycle the hydrogen-rich vapour phase, the liquid phase being directed into a stripper using vapour, which permits the

separation at the head, on the one hand, of the gases rich in  $\text{H}_2\text{S}$  (which are treated so as to extract the sulphur) and, on the other hand, the light hydrocarbons ("wild petrol"), and desulphurized gas oil at the bottom.

The problem confronting the oil-refining industry, in the face of increasingly strict specifications for products in respect of their sulphur content, was partly resolved by a substantial increase in the volume of catalyst used; in practical terms, this translated into the extension of a plurality of reactors in series, thus making it possible to achieve desulphurization rates of the order of 95 to 98 %, for example in respect of diesel fuel. Nevertheless, in order for this process to be optimal, fractional distillation is required after each reactor, in order to eliminate, in particular, the  $\text{H}_2\text{S}$  produced during desulphurization, the introduction of which  $\text{H}_2\text{S}$  into the following reactor would adversely affect its desulphurization efficiency, and it would also be necessary to extract, from the effluents from the preceding reactor, those effluents with a sulphur content which meets the specifications, such that the capacity of the following reactor is not loaded needlessly. All the foregoing measures increase costs considerably.

It is also known, in particular from International Application WO 94/09090 (Mobil), to use a process for improving the quality of the naphtha and light fuel fractions obtained by catalytic cracking and having a high content of sulphur compounds; said process comprises a first sweetening step (by oxidation of the mercaptans), followed by a fractional distillation step separating the effluents into a low boiling-point fraction, free of mercaptans, and a fraction having a higher boiling point and a high sulphur and thiophenic-compound content; said second fraction is then subjected to a hydrodesulphurization process by passing through a reactor, followed by a step in which the octane content is restored in another reactor containing an acid catalyst, without intermediate fractional distillation; it is possible for the mercaptans to be withdrawn from the effluents from the second reactor by passing into an extraction unit. Accordingly, this involves a complex and costly installation.

There is a solution to the problem of extracting the  $\text{H}_2\text{S}$  gas produced between two reactors, but this process is costly; yet this is proposed in International Application WO 96/17903 (Davy Process Technology) which describes a two-stage process for the hydrodesulphurization of a hydrocarbon charge, comprising an operation to strip the effluents from the reactor or reactors of the first stage, by a recycle gas containing hydrogen so as to separate  $\text{H}_2\text{S}$  produced during the desulphurization process, from the liquid fraction which is directed to the second stage.

It does, however, appear that the effectiveness of such desulphurization processes is open to considerable improvement, in particular with regard to the economics thereof.

It is thus that a novel solution, making it possible to overcome the problems associated with the limitation in the capacity of hydrotreating reactors, proved to be particularly interesting, by using a specific fractional distillation according to the invention.

According to the invention, it was, in fact, noted with surprise that, using a fractional distillation unit by means of which it is possible to distil, simultaneously, a plurality of hydrocarbon charges, and which is designed in a manner so as to separate the liquid bottom fractions from each of said charges, it was possible to improve the quality of the end products and, in particular, to reduce their sulphur content, without incurring excessive increases in the operating costs of the reactor.

The transformation of such a unit being relatively simple to carry out, the present invention thus relates to a simple process which can be used in existing installations and necessitates only a minimal adaptation, which reduces the capital outlay involved.

More particularly, the invention relates to a hydrotreating process for a hydrocarbon charge using at least one hydrotreating reactor, in particular a hydrodesulphurization reactor, and a fractional distillation unit comprising two separate injection zones for the hydrocarbon charges, a common zone for the vaporization of the distillate or light fractions, and two separate withdrawing means for the liquid bottom fractions; according to the invention, the hydrocarbon charge is injected for fractional distillation into the first injection zone, the liquid bottom fraction from the corresponding withdrawing means is directed to the hydrotreating reactor, and the effluents from said reactor are injected into the second injection zone for fractional distillation, while the distillates or light fractions are discharged from the common zone via an evacuation means, and that the heavy liquid bottom fraction corresponding to the second injection zone is extracted via the corresponding withdrawing means.

According to a particular embodiment of the invention, it is possible for the hydrocarbon charge to be a petrol fraction, a kerosene fraction, gas oils or vacuum distillates.

In a preferred embodiment of the invention, the liquid bottom fractions from said injection zones of the fractional distillation unit are isolated from each another by means of partitioning disposed

within the fractional distillation unit.

According to a different embodiment, the partitioning is vertical or horizontal.

The distillates, or light fractions, discharged from the common zone via the evacuation means have a sulphur content lower than or equal to a predetermined limiting value; thus, only that fraction, the sulphur content of which is to be corrected, is directed to the hydrotreating reactor, this resulting in a reduction in the spatial requirement.

Advantageously, the initial hydrocarbon charge is subjected to a pre-treatment, either in a second hydrodesulphurization reactor, the operating conditions (pressure, temperature, hourly space velocity of the charge, or VVH, type of catalyst, etc.) of which may differ, or in a sweetening device, or in a sulphur trap.

Advantageously, the distillates or light fractions discharged from fractional distillation by head evacuation are treated in a specific reactor, depending on the content of residual sulphur or aromatic compounds contained therein; the catalyst used in said reactor is different from that used in the first reactor, and is based on platinum or is of a thioresistant type (resistant to sulphur).

The invention also relates to an apparatus for the hydrotreating of a hydrocarbon charge, which apparatus includes at least one hydrotreating reactor, a fractional distillation unit disposed between the feeding means for said hydrocarbon charge and said hydrotreating reactor, as well as supply ducts for hydrocarbon charge and the effluents from the hydrotreating reactor to the fractional distillation unit, said apparatus being characterized in that the fractional distillation unit comprises separating means which define two separate zones, the supply duct for the hydrocarbon charge opening into one of said zones, and the supply duct for the effluents from the reactor opens into the other of said zones, and in that the fractional distillation unit has two different withdrawal means via which the liquid bottom fractions from the hydrocarbon charge and the effluents from the reactor are extracted respectively.

In an advantageous embodiment, the separating means are formed by vertical partitions which extend from the bottom of the fractional distillation unit; advantageously, said partition is formed by a cylindrical element disposed within and, preferably, concentrically with the vertical wall of the fractional distillation unit. It is also possible for the partition to be formed by a wall disposed

in a plane which is parallel to the longitudinal axis of the fractional distillation unit.

According to another embodiment, the separating means are horizontal, and the two supply ducts, respectively for the hydrocarbon charge and for the effluents from the reactor, open up at different levels of the fractional distillation unit.

The horizontal separating means are preferably formed by a plate provided with at least one funnel.

It is advantageously possible for the fractional distillation unit to be disposed between two hydrodesulphurization reactors, or between a sweetening reactor and a hydrodesulphurization reactor; in addition, it is possible to feed via the head evacuation means for the distillates or light fractions, a further reactor having a more specific action as a function depending on the residual sulphur content or aromatic-compound content in said distillates or light fractions.

Other characteristic features and advantages of the invention are set out in the description of embodiments which are given with reference to the attached drawings, in which:

- Figure 1        shows a first embodiment of an apparatus according to the invention,  
Figure 2        shows a second embodiment of an apparatus according to the invention,  
Figures  
3 and 4        show two variations of the fractional distillation unit illustrating other options for providing the partitioning in the fractional distillation unit according to the invention.

The hydrotreating apparatus as illustrated diagrammatically in Figure 1, essentially comprises a fractional distillation column or unit 3, having a cylindrical shape, provided with plates similar to those provided in a distillation column, and fitted with a partition element 12, which extends vertically from the bottom of the column up to a predetermined height and being in the form of a wall disposed in a plane parallel to the longitudinal axis of said column; as a result of this arrangement, it is possible to subdivide the corresponding volume of said column 3 into two separate and distinct injection zones 4 and 5 and a common upper vaporization zone 8 for the distillates or light fractions; the hydrocarbon charge 1 to be treated is introduced via the line 9 into the first distinct zone 4 of the fractional distillation column 3, the operation of which is

adjusted in a manner so as to extract, via the line 11, the head distillates or fractions having a predetermined final distillation point and a sulphur content in accordance with a fixed value, or even lower than or equal to a predetermined limiting value; the liquid bottom fraction of the charge 1 is extracted from the bottom of the zone 4 via the line 6 and is directed into a hydrodesulphurization reactor 2, the operating conditions (pressure, temperature, type of catalyst used, the ratio per unit volume  $H^2$ /charge, i.e. the ratio of the hourly input of treatment hydrogen in  $Nm^3$  (standard  $m^3$ )/h relative to the hourly input of charge in  $m^3$ /h, the hourly space velocity of the charge or VVH, i.e. the ratio of the hourly input of charge in  $m^3$ /h relative to the volume of catalyst in  $m^3$ ) of which are determined according to the nature of the charge 1 and its sulphur content; the effluents from this reactor 2 are injected, via the line 10, into the second separate zone 5 of the fractional distillation column 3, a portion of said effluents being extracted in the form of a distillate or light fraction via the line 11, while the corresponding liquid bottom fraction is withdrawn via the line 7; it is also possible for this fraction to have a low sulphur content, as will be shown in the attached Examples.

Figure 2 shows a hydrotreating apparatus which differs from the preceding apparatus only in that the hydrocarbon charge 1 is subjected to a pre-treatment in a reactor 20, the effluents therefrom being introduced via the line 9 into the first zone 4 of the fractional distillation column 3; depending on the nature of the charge 1, it is possible for the reactor 20 either also to be a hydrodesulphurization reactor working under different operating conditions, or to be a sweetening reactor, or any other apparatus which permits a reduction of the sulphur content (sulphur trap); in addition, shown in broken lines, is an optional third reactor 30, by means of which it is possible to treat the distillates or light fractions from fractional distillation 3 via the evacuation means 11, in a more specific manner, for example as a function depending on their residual sulphur content or aromatic-compound content (for example, benzene), by using appropriate catalysts (in particular platinum-based or thioresistant).

Figure 3 shows a first variation of an embodiment of the partition in the fractional distillation column 3; said partition comprises a cylindrical element 22 disposed within and concentric with the wall 23 of the column 3 and extending from the bottom 24 of said column up to a predetermined height, in a manner so as to delimit a first separate zone 4 which receives, via the line 9, the hydrocarbon charge 1 or its effluents after passing through a reactor (not illustrated, but identical to the reactor 20 of Figure 2), and a second separate zone 4 which receives, via the line 10, the effluents from the hydrotreating reactor (not illustrated, but identical to the reactor 2

of Figures 1 and 2); the liquid bottom fractions from these two zones 4 and 5 are extracted via the lines 6 and 7, respectively, the bottom fraction extracted via the line 6 feeding the hydrotreating reactor; it should be noted that it is possible for the feed lines 9 and 10 to be interchanged with regard to zones 4 and 5, without affecting the operation of the column 3, provided that the corresponding withdrawal lines 6, 7 are also interchanged.

Figure 4 shows a second variation of an embodiment of the partition in the fractional distillation column 3; said partition comprises a plate 34 disposed horizontally and in circular and tight contact with the wall 23 of the column 3, which is provided with at least one funnel 35, thus permitting the passage of distillates or light fractions of the hydrocarbon charge introduced via the line 9 into the zone of the column 3 situated below the plate 34, and their head evacuation via the line 11; in addition, said plate 34 makes it possible to separate, from the liquid bottom fraction of the hydrocarbon charge introduced via the line 9, the liquid bottom fraction from the effluents from a reactor, which is not illustrated (but similar to the reactor 2 of Figures 1 and 2), introduced via the line 10 into a zone of the column 3 situated above the plate 34, and to withdraw said fraction via the line 7; it will also be noted that it is possible for the hydrocarbon charge to be introduced, via the line 9, into the zone of the column 3 situated above the plate 34, and that it is possible for the effluents from the reactor to be introduced, via the line 10, below the plate 34, without adversely affecting the operational effectiveness of the column 3, provided that the withdrawal lines 6 and 7 are interchanged.

Without exceeding the scope of the invention, it is also conceivable to provide a hydrotreating apparatus which differs from that illustrated in and described with reference to Figure 2 only in that the reactor 2 is designed to have a more specific de-aromatization action (by using a platinum-based or thioresistant catalyst), or a paraffin-removing action, in a manner so as to treat the charges 1 which may, in particular, be heavy petrols from catalytic cracking, and to withdraw, via the line 7, a fraction for aviation fuel which meets the specifications.

The Examples below aim to illustrate the invention.

#### Example 1

Use is made of a broad fraction from a Brent-type crude, having an initial distillation point of 150° C and a final distillation point of 360° C, and the sulphur content of which is 0.12% by mass; said fraction is introduced, according to Figure 1, via the duct 9, into the first zone 4 of the

fractional distillation unit 3, from which is extracted, via the duct 11, a head fraction having an initial distillation point of 240° C and a sulphur content of less than 0.018 % by mass; this fraction is used as base for VLSC gas oil (very low sulphur content).

Via the duct 6, a liquid bottom fraction is extracted from the first zone 4 and this has an initial distillation point of 220° C and a sulphur content of 0.2 % by mass; said fraction is then treated in a hydrodesulphurization reactor 2, the operating conditions of which are as follows:

- catalyst: NiMo HR348, marketed by Procatalyse
- temperature: 340° C
- pressure: 50 bars
- ratio per unit volume H<sub>2</sub>/charge: 150 Nm<sup>3</sup>/m<sup>3</sup>
- hourly space velocity (VVH): 1.5 h<sup>-1</sup>.

The effluents from this reactor are injected, via the duct 10, into the second separate zone 5 of the fractional distillation unit 3, a portion of said effluents being collected in the form of a distillate via the duct 11 at the head of fractional distillation 3, while the liquid bottom fraction of said effluents is withdrawn via the duct 7; said fraction has an initial distillation point of 220° C, a final distillation point of 360° C and a sulphur content of 0.004 % by mass (40 ppm), which makes it suitable for use as an "ecological" gas oil ("city gas oil").

By way of comparison, in order to obtain an equally substantial desulphurization of the same fraction, without using fractional distillation according to the invention, the operating conditions of the hydrodesulphurization reactor being identical (in particular VVH = 1.5 h<sup>-1</sup>), it is necessary to use an additional catalyst volume of 60 %, hence the clear economic advantage of the invention.

### **Example 2**

The charge used in this example is a gas oil fraction from direct distillation ("straight-run"), having a sulphur content of 1.2 % by mass, an initial distillation point of 150° C and a final distillation point of 380° C.

This charge is introduced, according to Figure 2, into a first hydrodesulphurization reactor 20 operating under the following conditions:

- catalyst: NiMo, HR348, marketed by Procatalyse
- temperature: 370° C



- pressure: 45 bars
- ratio per unit volume  $H_2$ /charge:  $200 \text{ Nm}^3/\text{m}^3$
- hourly space velocity (VVH):  $2 \text{ h}^{-1}$ .

The effluent from the reactor is introduced, via the duct 9, at a temperature of  $370^\circ \text{ C}$ , into the first zone 4 of the fractional distillation unit 3, from which is collected, via the duct 11, a head fraction which has an initial distillation point of  $130^\circ \text{ C}$ , containing less than 0.03% by mass of sulphur, and which enters the composition of the gas oils; in addition, via the duct 6, a liquid bottom fraction having an initial distillation point of  $300^\circ \text{ C}$  and containing 0.3% by mass of sulphur, is also collected.

This bottom fraction is directed, via the duct 6, to the inlet of a second hydrodesulphurization reactor 2, the operating conditions of which are as follows:

- catalyst: NiMo, HR348, marketed by Procatalyse
- temperature:  $360^\circ \text{ C}$
- pressure: 40 bars
- ratio per unit volume  $H_2$ /charge:  $150 \text{ Nm}^3/\text{m}^3$
- hourly space velocity (VVH):  $1.5 \text{ h}^{-1}$ .

The effluents from the reactor 2 are collected via the duct 10, and said effluents, containing 0.025% by mass of sulphur, are injected into the second separate zone 5 of the fractional distillation unit 3, a portion of said effluents is collected in the form of a distillate via the duct 11; in addition, the liquid bottom fraction from said second zone 10 [sic.] is withdrawn via the duct 7, said liquid bottom fraction having an initial distillation point of  $300^\circ \text{ C}$  and a final distillation point of  $380^\circ \text{ C}$  and containing 0.027% by mass of sulphur. It is possible for this product to be used as a base for gas oil.

By way of comparison, in order to ensure an equally high-powered desulphurization of the same gas oil fraction, in an installation comprising the reactors 20 and 2 arranged in series, operating under the same conditions as those set out above, with a standard fractional distillation unit interposed between said two reactors, it is necessary to add a second fractional distillation unit after the second reactor, in particular of the stripper type; it is thus evident that the fractional distillation according to the invention ensures substantial economic advantages.

**Example 3**

The charge used is a "straight-run" distillate fraction, having an initial distillation point of 145° C and a final distillation point of 300° C, and a sulphur content of 0.5% by mass, partly in the form of mercaptans in the head of the fraction.

Said charge is introduced, according to Figure 2, into a first sweetening reactor 20 (by oxidation of the mercaptans on a fixed bed).

The effluent from the reactor is introduced, via the duct 9, into a first zone 4 of a fractional distillation unit 3, from which is collected, via the duct 11, a head fraction having an initial distillation point of 140° C, containing less than 0.1% by mass of sulphur and which is used as aviation fuel.

Withdrawn via the duct 6 is a liquid bottom fraction, having an initial distillation point of 230° C, containing 0.8% by mass of sulphur, the mercaptans having been converted into disulphides in the first reactor and said disulphides being carried in said heavy bottom fraction; this fraction is introduced into a hydrodesulphurization reactor 2 (HDS), the operating conditions of which are as follows:

- catalyst: CoMo, HR316, marketed by Procatalyse
- temperature: 320° C
- pressure: 35 bars
- ratio per unit volume H<sub>2</sub>/charge: 100 Nm<sup>3</sup>/m<sup>3</sup>
- hourly space velocity (VVH): 4 h<sup>-1</sup>.

The effluents from this reactor are collected via the duct 10, and said effluents, containing 0.02% by mass of sulphur, are injected into a second separate zone 5 of the fractional distillation unit 3, a portion of said effluents being collected in the form of a distillate via the duct 11 at the head of fractional distillation 3; the liquid bottom fraction from said second zone 5 is also withdrawn via the duct 7 and has an initial distillation point of 230° C, a final distillation point of 300° C and contains 0.025% by mass of sulphur; it is possible to use this fraction as a base for gas oil.

As in Example 2, in order to obtain an equally substantially desulphurization of the same fraction, using a standard intermediate fractional distillation, the operating conditions of the sweetening and hydrodesulphurization reactors being identical, it is necessary to add a fractional distillation, for

example of the "stripper" type, downstream of the second reactor, hence the economical significance of the process according to the invention.

## CLAIMS

1. Hydrotreating process for a hydrocarbon charge (1), using at least one hydrotreating reactor (2), in particular a hydrodesulphurization reactor, and a fractional distillation unit (3), said fractional distillation unit (3) comprising two separate injection zones (4, 5) for the hydrocarbon charges, a common zone (8) for the vaporization of the light fractions, and two separate withdrawing means (6, 7) for the liquid bottom fractions, said process being characterized in that:

- the hydrocarbon charge (1) is injected for fractional distillation (3) into the first injection zone (4),
- the liquid bottom fraction from the withdrawing means (6) of the injection zone (4) is directed to the hydrotreating reactor (2),
- the effluents from said reactor (2) are injected into the second injection zone (5) for fractional distillation (3),
- the light fractions are discharged from the common zone (8) via an evacuation means (11),
- the heavy liquid bottom fraction corresponding to the second injection zone (5) is extracted via the withdrawing means (7).

2. Process according to claim 1, characterized in that the hydrocarbon charge (1) is a petroleum fraction, a kerosene fraction, gas oils, or vacuum distillate.

3. Process according to claim 1 or claim 2, characterized in that the liquid bottom fractions from said injection zones (4, 5) of the fractional distillation unit (3) are isolated from each another by means of a partition (12) disposed within the fractional distillation unit (3).

4. Process according to claim 3, characterized in that the partition is vertical or horizontal.

5. Process according to any one of the preceding claims, characterized in that the light fractions, discharged from the common zone (8) via the evacuation means (11), have a sulphur content lower than or equal to a predetermined limiting value.

6. Process according to any one of the preceding claims, characterized in that the

hydrocarbon charge (1) is subjected to a pre-treatment, either in another hydrodesulphurization reactor (20), the operating conditions (P, T, VVH) of which may be different, or in a sweetening device, or in a sulphur trap.

7. Process according to any one of the preceding claims, characterized in that the light fractions, discharged from the fractional distillation unit (3) via the evacuation means (11), are treated in a specific reactor (30), depending on their residual sulphur content therein.

8. Process according to claim 7, characterized in that the catalyst used in the reactor (30) is different from that used in the reactor (2) and is platinum-based or is thioresistant.

9. Apparatus for the hydrotreating of a hydrocarbon charge (1), which apparatus includes at least one hydrotreating reactor (2), a fractional distillation unit (3) disposed between the feeding means for said hydrocarbon charge (1) and said hydrotreating reactor (2), as well as supply ducts (9, 10) for the hydrocarbon charge and the effluents from the hydrotreating reactor (2) to the fractional distillation unit (3), said apparatus being characterized in that

- the fractional distillation unit (3) comprises separating means (12, 22) defining two separate zones (4, 5), the supply duct (9) for the hydrocarbon charge (1) opening into one (4) of said zones (4, 5), and the duct (10) for the effluents from the hydrotreating reactor (2) opens into the other (5) of said zones (4, 5), and in that
- the fractional distillation unit (3) has two different withdrawal means (6, 7) via which the liquid bottom fractions from the hydrocarbon charge (1) and the effluents from the reactor (2) are extracted respectively.

10. Hydrotreating apparatus according to claim 9, characterized in that the separating means are formed by a vertical partition (12, 22) extending from the bottom (25) of the fractional distillation unit (3).

11. Hydrotreating apparatus according to claim 10, characterized in that the partition is formed by a cylindrical element (22) disposed within and, preferably, concentrically with the vertical wall (23) of the fractional distillation unit (3).

12. Hydrotreating apparatus according to claim 9, characterized in that the separating means are horizontal, and in that two supply ducts (9, 10) respectively for the hydrocarbon charge

and the effluents from the reactor (2) open up at different levels of the fractional distillation unit (3).

13. Hydrotreating apparatus according to claim 12, characterized in that the horizontal separating means are formed by a plate (34) provided with at least one funnel (35).

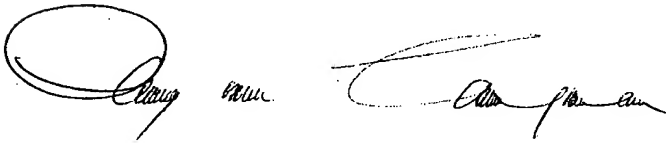
14. Hydrotreating apparatus according to any one of claims 9 to 13, characterized in that the fractional distillation unit (3) is, moreover, preceded by a hydrodesulphurization reactor (20) and in that the reactor (2) is a hydrodesulphurization reactor.

15. Hydrotreating apparatus according to any one of claims 9 to 13, characterized in that the fractional distillation unit (3) is preceded by a sweetening reactor (20) and in that the reactor (2) is a hydrodesulphurization reactor (2).

16. Hydrotreating apparatus according to any one of claims 9 to 15, characterized in that it additionally comprises a further reactor (30) in which the light fractions extracted from the fractional distillation unit (3) via the evacuation means (11) are treated, said reactor (30) having a more specific action, depending on the residual sulphur content or the aromatic-compound content of said light fractions.

CERTIFICATE

I, CORDULA IRENE MAY VON LANGENAU, being a Sworn Translator of the Supreme Court of South Africa (Transvaal Provincial Division) for the French and English languages, of Adams & Adams Place, 1140 Prospect Street, Hatfield Pretoria,  
HEREBY CERTIFY THAT, to the best of my knowledge and belief, the attached document is a true, correct and complete translation of French Patent Application No. 96 16290 in the name of **TOTAL RAFFINAGE DISTRIBUTION S.A.**, and of the covering Certificate, issued by the French National Institute for Industrial Property on 22nd December, 1997.



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Cordula Irene May von Langenau  
Sworn Translator

Pretoria  
29th May, 1998